A Mössbauer study of hyperfine interactions in the boroferrite $\text{Fe}_{3-x}\text{Ga}_x\text{BO}_6$ ($x = 0, 0.12$)

M VITHAL, R JAGANNATHAN and N RAVI

School of Chemistry, University of Hyderabad, Hyderabad 500 134, India

Abstract. Fe_3BO_6 shows no thermal hysteresis around the phase transition temperature $T_{\text{SR}} = 418$ K; $\text{Fe}_{2.88}\text{Ga}_{0.12}\text{BO}_6$ undergoes spin transition at $T_{\text{SR}} = 403$ K resulting in a reduction of the T_{SR} . Both these features are different from the reported observations on $\alpha\text{-Fe}_2\text{O}_3$. The two Fe^{3+} sites show difference in their magnetic interactions. Ga^{3+} replaces Fe^{3+} in a random manner.

Keywords. Spin-reorientation; thermal hysteresis; biquadratic exchange interaction; random distribution model; boroferrite; Mössbauer study; hyperfine interactions.

1. Introduction

Boroferrites occur in a variety of structures giving rise to materials like boracite, ludwigite warwickite, etc., which have modifications in structures resulting in interesting electrical and magnetic properties. The present work deals with a detailed study of the simple and substituted boroferrite, Fe_3BO_6 . In this system boron has the unusual tetrahedral coordination. It is known to exhibit spin reorientation and the mechanism of spin reorientation is of considerable interest. In addition to a study of the behaviour of metal sites with regard to their magnetic interaction and the spin reorientation behaviour on substitution we also present here an analysis of the Mössbauer spectra of the substituted compounds on the basis of random distribution model (Coe and Sawatzky 1971).

2. Experimental procedure and characterization

The compounds were prepared from the stoichiometric mixture of metal nitrates and 400 % excess boric acid as described by Muller *et al* (1978). Mössbauer measurements were made as described earlier (Ravi *et al* 1982). The IR and x-ray analysis confirmed the product formation and their purities.

3. Results and discussion

The Mössbauer spectra of Fe_3BO_6 were recorded in the range 77–520 K. The room temperature Mössbauer spectrum of Fe_3BO_6 yields two well-resolved six-line patterns superimposed on each other with relative intensities of the two sextets in the ratio 2:1. The spin reorientation (T_{SR}) and Curie temperatures (T_c) are 418 and 518 K respectively. The spin reorientation is identified by abrupt and well-characterised changes in the line splittings of the Mössbauer spectra below and above T_{SR} for the two sites (figure 1). The

plots of reduced hyperfine fields *vs* reduced temperatures are shown in figure 2. It is found that one of the sites follows the Brillouin behaviour for $S = 5/2$ whereas the fields for the other site deviates significantly. Such a deviation from the Brillouin curve can be accounted for by the inclusion of the higher order biquadratic exchange term as discussed later.

The Mössbauer spectra of $\text{Fe}_{2.88}\text{Ga}_{0.12}\text{BO}_6$ were recorded in the range 77–494 K. This sample is also found to undergo spin reorientation as shown by the line splittings. The T_{SR} and T_c are 403 and 494 K respectively. A decrease in spin reorientation temperature on substitution is in contrast with that observed in $\alpha\text{-Fe}_2\text{O}_3$ by Dezsi *et al*

Figure 1. Mössbauer spectra of Fe_3BO_6 (a) below and (b) above T_{SR} .

Figure 2. Reduced hyperfine field *vs* reduced temperature in Fe_3BO_6 . Solid spheres and crosses are experimental points for the 8*d* and 4*c* sites respectively. Solid line (a) is the theoretical Brillouin curve for $S = 5/2$ and (b) for $S = 5/2$ including biquadratic exchange $j/J = 0.015$.

(1967) where Rh^{3+} substitution increases the T_{SR} . The Brillouin behaviour of the two sites in this sample is similar to that of the parent material. The room temperature Mössbauer spectrum of $\text{Fe}_{2.88}\text{Ga}_{0.12}\text{BO}_6$ results in significant line broadening and lowering of the internal magnetic field compared to the parent material. The spectrum of the substituted compound may be analysed assuming a random replacement of the magnetic Fe^{3+} ion by the non-magnetic Ga^{3+} ion. Such an analysis enables testing the applicability of the model by comparing the experimental spectrum with theory and obtaining the information on exchange interaction. The computer-simulated spectrum along with the experimental spectrum is given in figure 3.

Spin reorientation can proceed in two ways: (i) the magnetic moment vector may rotate continuously and coherently from the x -axis to z -axis (b) the magnetic moment vector jumps discontinuously from x -axis to z -axis. The former is explained by Landau's theory of second-order phase transition as illustrated in the case of ErFeO_3 (Grant and Geller 1969). In $\alpha\text{-Fe}_2\text{O}_3$, where a thermal hysteresis behaviour is observed for over a temperature range of 15° , process (b) has been invoked (Nininger and Schroerer 1978). An analysis of the Mössbauer data for the behaviour of isomershift, quadrupole splitting and effective hyperfine field as a function of temperature in the vicinity of T_{SR} shows that these values are reproducible for a given temperature irrespective of whether the measurements are made during heating or cooling in a cyclic manner. Thus in Fe_3BO_6 and $\text{Fe}_{2.88}\text{Ga}_{0.12}\text{BO}_6$ thermal hysteresis is absent. Such a behaviour is in accordance with spin reorientation taking place as a second-order phase transition *viz.*, rotation of the magnetic moment vector continuously from x -axis to z -axis. This result also agrees with that of Voigt (1975) who based his conclusion on susceptibility and field-induced phase transition studies.

Fe_3BO_6 is known to have orthorhombic symmetry with space group Pnma , the temperature dependence of the hyperfine field corresponding to the $8d$ site follows

Figure 3. Comparison of (a) experimental Mössbauer spectrum at 296 K with (b) theoretical spectrum based on the random substitution model.

closely the Brillouin behaviour. On the other hand the 4c site gives rise to consistently higher values of $H_{\text{eff}}(T)/H_{\text{eff}}(0)$ than that predicted by molecular field theory. This type of behaviour has been attributed to the significant contribution due to the biquadratic exchange term of the form

$$J \cdot S_a S_b - j (S_a S_b)^2,$$

where $J > 0$ and the magnitude of j can differ depending upon the superexchange interaction (Rodbell *et al* 1967). The theoretical curve with a j/J 0.015 shows close agreement with experimental data for the 4c site. Similar values for j/J have been obtained in oxide lattices such as NiO and LiFeO₂ (Bhide and Shenoy 1966; Cox *et al* 1963).

For an analysis of the Mössbauer spectra of Fe_{2.88}Ga_{0.12}BO₆ on the basis of random distribution model (Coey and Sawatzky 1971) the internal magnetic fields were calculated assuming a binomial distribution for different possible near-neighbour environments for a given concentration of nonmagnetic ion. The fields corresponding to each near neighbour environment ($\sigma(Z)$) are given by

$$\sigma(Z) = \beta_s \left(\frac{3S \langle \sigma \rangle_{\text{av}} Z}{(S+1) \langle Z \rangle_{\text{av}} \tau} \right)$$

where τ is related to the exchange constant J by $\tau = 3kT/2S(S+1)J \langle Z \rangle_{\text{av}}$. It is found that the spectrum simulated for $\tau = 0.7$ agreed quite well with experimental spectrum (figure 3) provided the quadrupole interaction is taken into account in computing the line positions. The agreement between the simulated and experimental spectrum shows that Ga³⁺ has no site preference between 4c and 8d. The exchange constant J is $\sim 10 \text{ cm}^{-1}$.

4. Conclusions

Fe₃BO₆ undergoes spin reorientation at 418 K. The non-observance of a break in the plots of hyperfine fields, isomer shift and quadrupole splitting *vs* temperature in the vicinity of T_{SR} suggests the absence of thermal hysteresis behaviour. Thus it is concluded that spin reorientation follows a second-order phase transformation. The temperature dependence of hyperfine field for the 8d site follows closely the Brillouin function for $S = 5/2$. The deviation of the 4c site from the Brillouin curve has been explained by including the biquadratic exchange interaction giving rise to $j/J = 0.015$. Substitution of Fe³⁺ by Ga³⁺ brings down T_{SR} from 418 to 403 K. It is found that Ga³⁺ has no site preference. An exchange constant $J \sim 10 \text{ cm}^{-1}$ has been obtained.

Acknowledgements

Financial assistance from UGC, New Delhi to MV and DST, New Delhi to NR is gratefully acknowledged.

References

- Bhide V G and Shenoy G K 1966 *Phys. Rev.* **143** 309
Coey J M D and Sawatzky G A 1971 *Phys. Status. Solidi.* **B44** 673

- Cox D E, Shirane G, Flinn P A, Ruby S L and Takei W J 1963 *Phys. Rev.* **132** 1547
Dezsi I, Erlaki G and Keszthelyi L 1967 *Phys. Status. Solidi.* **21** K121
Grant R W and Geller S 1969 *Solid State Commun.* **7** 1291
Muller O, O'Horo M P and O'Neill J F 1978 *J. Solid State Chem.* **23** 115
Nininger R C Jr and Schroerer D 1978 *J. Phys. Chem. Solids.* **39** 137
Rodbell D S, Jacobs I S, Owens J and Hanis E A 1967 *Phys. Rev. Lett.* **11** 245
Ravi N, Jagannathan R, Rama Rao B and Raza Hussain M 1982 *Inorg. Chem.* **21** 1019
Voigt C 1975 *Phys. Lett.* **A53** 223